

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 11/15/95	3. REPORT TYPE AND DATES COVERED Final 9/15/92-9/14/95	
4. TITLE AND SUBTITLE Static and Mobile Polymer Surfaces of Well Defined Structure		5. FUNDING NUMBERS DAAL03-92-G-0402	
6. AUTHOR(S) William J. Brittain, Wayne L. Mattice & Mark D. Foster			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Polymer Science The University of Akron Akron, OH 44325-3909		8. PERFORMING ORGANIZATION REPORT NUMBER Report No. 4	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING/MONITORING AGENCY REPORT NUMBER ARO 30880.4-MSM	
11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Photoresponsive monolayers were prepared by the chemisorption of azobenzene-containing molecules to silicate substrates. A reversible change in the water contact angle was observed upon UV irradiation. Neutron reflectometry was used to probe protein adsorption to monolayers. The adsorption of human serum albumin was observed for amine- and methyl-terminated monolayers. Molecular dynamic simulations indicated directions for the next generation of synthetic efforts; the ideal placement for the azobenzene group is near the tail or head of the surface-reactive molecule.  DTC QUALITY INSPECTED 4			
14. SUBJECT TERMS smart surfaces, monolayers, photoresponsive surface, protein adsorption, neutron reflectometry		15. NUMBER OF PAGES 5	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

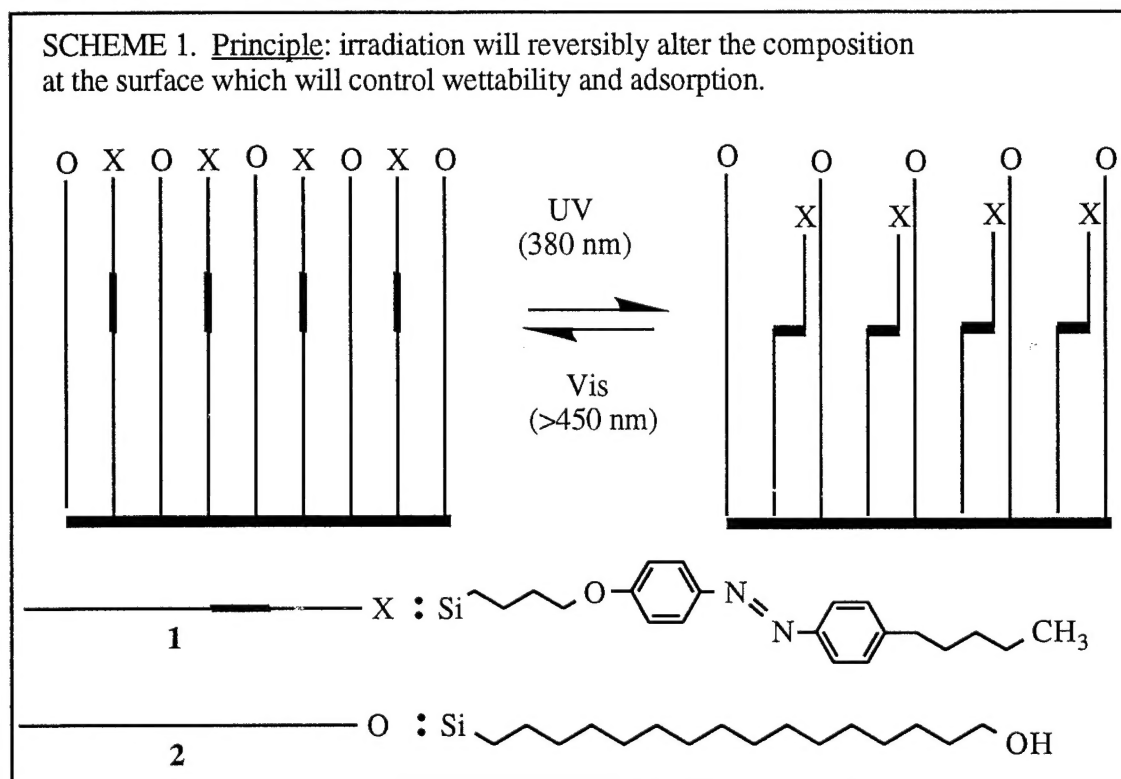
19960209 044

# STATIC AND MOBILE POLYMER SURFACES OF WELL-DEFINED STRUCTURE FINAL REPORT

William J. Brittain, Wayne L. Mattice and Mark D. Foster  
DAAL03-92-G-0402  
November 15, 1995

## PROBLEM STUDIED

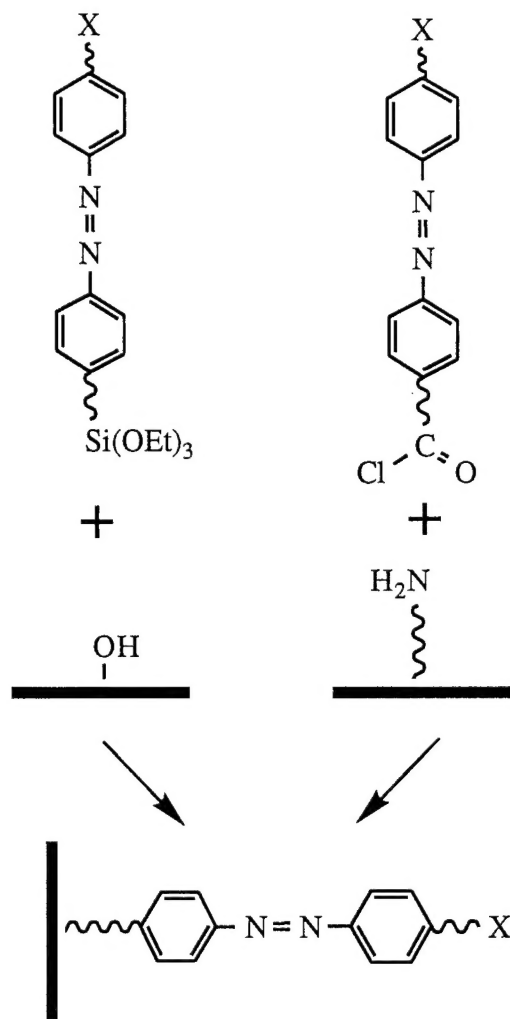
Photoactive self-assembled monolayers (SAMs) containing azobenzene chromophores were prepared and studied (see Scheme 1). The photoresponsive group induced reversible changes in the wettability of the surface depending on whether the surface is exposed to visible or ultraviolet light. Because protein adsorption is tied to wettability, protein adsorption studies utilizing self-assembled monolayers were performed. Molecular modeling of azobenzene SAMs revealed important structural considerations for the optimization of the photoresponsive effect.



## SUMMARY OF MOST IMPORTANT RESULTS

### Synthesis of Photoactive Monolayers

Scheme 2 depicts the two synthetic approaches to azobenzene monolayers that produced the best photoresponsive effect. One involved the direct deposition of triethoxysilanes and the second was the in situ functionalization of amine-terminated SAMs with azobenzene derivatives containing an acid chloride group.



Scheme 2. Synthetic Approaches to Photoactive SAMs

Highlights of this synthetic work include:

- SAMs containing azobenzene were fully characterized using a combination of ATR-IR spectroscopy, water contact angles, ellipsometry, X-ray reflectometry, and ESCA.
- Characterization was consistent with the attachment of azobenzene to the surface. However, X-ray reflectometry indicated a film thickness that was approximately 40-50% of the calculated film thickness for fully extended chains. The X-ray results suggest that film coverage was less than 100%.
- SAMs were prepared where the terminal functional group was either a hydrogen or a pentyl group ( $X = \text{H}, \text{C}_5\text{H}_{12}$  in Scheme 2). The length of the spacer between the azo linkage and the surface was also varied. The photoresponsive effect was measured by the change in the water contact angle upon exposure to 365 nm light. Under ambient conditions (normal interior lighting), the contact angle of an azobenzene SAM ranged from 75-85 degrees. Exposure effected a 5-10 degree decrease in the water contact angle. This decrease was reversible for many cycles.

- Attempts to prepared mixed monolayers according to Scheme 1 were unsuccessful.

### In-situ Study of Protein Adsorption to Functionalized SAMs

Novel in situ neutron reflectivity investigation of the absorption of HSA from solution onto functionalized SAM surfaces confirmed that the absorption of a proteins to a tailored surface could be varied using the synthetic techniques developed in this project. An important contribution was also made to the general field of adsorption characterization, as the spatial resolution offered by the in situ reflectivity measurements is improves upon that previously available by several orders of magnitude. In a collaborative effort involving scientists at the National Institute of Standards and Technology's Reactor Radiation Division and Becton Dickinson we have quantified differences in the near interface composition profiles for HSA in solutions next to  $-\text{CH}_3$ ,  $-\text{NH}_3^+$ , and silicon oxide surfaces. This approach collects information on the solution-surface interaction while the surface is in a biologically relevant state. Complementary NR measurements made using variable scattering contrast as well as X-ray reflectometry measurements of the functionalized monolayers themselves before exposure to solution were key to refining concentration profiles from the data.

While no adsorption is detected at the native oxide of silicon, adsorption does occur for both the  $-\text{CH}_3$ , and  $-\text{NH}_3^+$  terminated surfaces. Both overall amount adsorbed in the protein rich layer next to the surface and the concentration immediately adjacent to the surface increased with bulk solution concentrations in the range from 0.005% to 0.1% HSA. Concentration profiles next to the  $-\text{NH}_3^+$  terminated surfaces consist of at least two distinct regions connected by a diffuse interface, as shown in Figure 1. The first region, immediately adjacent to the surface, presents a plateau in concentration at a level more than two orders of magnitude higher than the bulk concentration. This region has a nominal thickness close to 4 nm, which is comparable to the smallest dimension of the protein's molecular envelope. A second region contains a very slowly decaying concentration at levels less than one tenth that of the very concentrated layer. No such second region is found for the concentration profiles next to the  $-\text{CH}_3$  terminated surfaces.

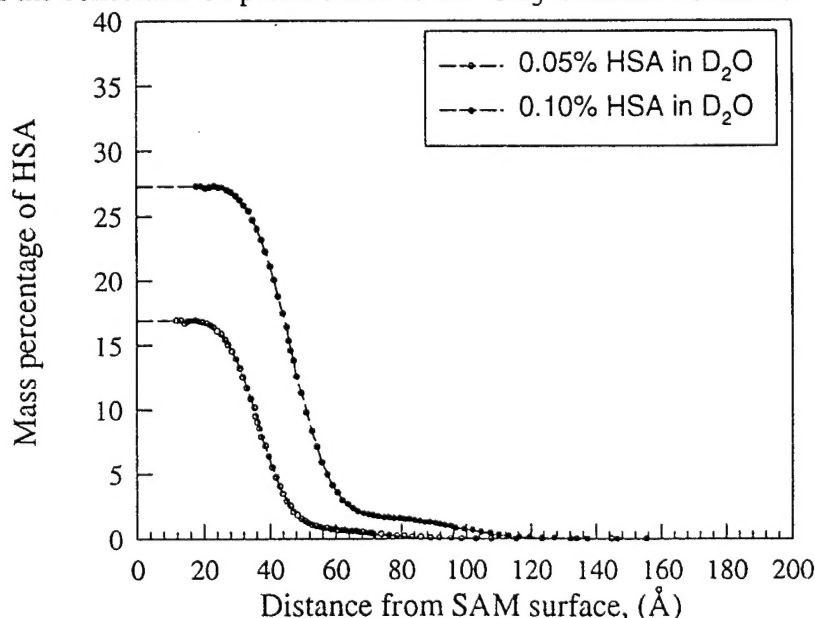


Figure 1. Composition profile of the interphase separating the bulk HSA solution and SAM surface derived from NR data for 0.05% and 0.1% HSA solutions.

### Molecular Dynamics Simulations of Azobenzene Monolayers

- Dense-packed SAMs (one chain for every 21 Å<sup>2</sup>) prepared with azobenzene in the *trans* conformation do not provide sufficient free volume for relaxation of the end-to-end distance of the chain when the azobenzene unit undergoes the photoinduced *trans*-to-*cis* isomerization.
- However, if the surface area accessible to the azobenzene is tripled, to 63 Å<sup>2</sup>, there is sufficient free volume for significant relaxation of the end-to-end distance of the chain when the azobenzene unit undergoes the photoinduced *trans*-to-*cis* isomerization. Merely doubling the accessible free volume (42 Å<sup>2</sup> per azobenzene-containing chain) is insignificant.
- The easiest way to insure that there is sufficient free volume for relaxation of the end-to-end distance in the chain with *cis* azobenzene is to prepare the SAM with the azobenzene-containing chain in the *cis* conformation, which implies preparing the SAM under uv irradiation.
- Therefore reversible photocontrol of the surface of the SAM will be marginal, at best, if the SAM is prepared under ordinary bench conditions (with the azobenzene in the *trans* conformation), but will be more impressive if the SAM is prepared under uv irradiation, with the azobenzene in the *cis* conformation.
- Slightly better performance might be expected for SAMs in which the azobenzene is placed near the head group, or near the tail, rather than in middle of the chain. However, this effect is not as important as the ones described above.

### LIST OF PUBLICATIONS AND TECHNICAL REPORTS

- "Synthesis and Characterization of a Photoactive Monolayer," L. M. Siewierski, L. M. Lander, A. Liebmann, W. J. Brittain and M. D. Foster, *SPIE Proceedings*, **2441**, 1 (1995).
- "Photoresponsive Monolayers," L. M. Siewierski and W. J. Brittain, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **36**(2), 158 (1995).
- "Friction and Wear of Surface-Immobilized C<sub>60</sub> Monolayers," L. M. Lander, W. J. Brittain, V. A. DePalma and S. R. Girolmo, *Chem. Mater.*, **7**, 1437 (1995).
- "Blood Contact Properties of Surface Immobilized C<sub>60</sub>," L. M. Lander, W. J. Brittain and E. A. Vogler, *Langmuir*, **11**, 375 (1995).
- "Atomic Force Microscopy of C<sub>60</sub> Tethered to a Self-Assembled Monolayer," V. V. Tsukruk, L. M. Lander and W. J. Brittain, *Langmuir*, **10**, 996 (1994).
- "Synthesis and Characterization of Self-Assembled Monolayers Containing Azobenzene," L. M. Siewierski and W. J. Brittain, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **35**(1), 490 (1994).
- "Molecular Dynamics Simulation of the Collapse of Poly(1,4-*trans*-butadiene) to a Globule and to a Thin film," Y. Zhan and W. L. Mattice, *Langmuir*, **27**, 7056 (1994).
- "Simulations of Self-Assembled Monolayers with the Same Surface Density but Different Grafting Patterns," *Langmuir*, **11**, 2103 (1995).
- "Atomistic Simulations of Self-Assembled Monolayers that Contain Azobenzene," L. Xing and W. L. Mattice *Polym. Mat. Sci. Eng. Prepr., Am. Chem. Soc., Div. Polym. Mat. Sci. Eng.*, **73**, 400 (1995).

"A Neutron Reflectometry Study of Human Serum Albumin Adsorption *In Situ*," A. Liebmann-Vinson, L. M. Lander, M. D. Foster, W. J. Brittain, E. A. Vogler, C. F. Majkrzak, S. Satija, *Langmuir*, accepted for publication, 9/95.

#### **PARTICIPATING SCIENTIFIC PERSONNEL**

Dr. Lorraine M. Lander, earned Ph.D. in Polymer Science, Dec. 1994.  
Ms. Lisa M. Siewierski, will earn Ph.D. in Polymer Science, Dec. 1995.  
Ms. Li Xing, graduate student  
Dr. Yongjian Zhan, postdoctoral  
Mr. Stas Petrash, Ph.D. Candidate in Polymer Science  
Ms. Nina Sheller, Ph. D. Candidate in Polymer Science  
Dr. Andrea Liebmann-Vinson, postdoctoral